

The University of Chicago

**THE ADDITION OF HYDROGEN CHLORIDE TO
ISOBUTYLENE**

**A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY**

DEPARTMENT OF CHEMISTRY

1942

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JOSEPH J. KATZ

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The Addition of Hydrogen Chloride to Isobutylene¹

BY JOSEPH J. KATZ^{2b}

The normal (Markovnikov) addition of halogen acids to alkenes is commonly supposed to proceed through the addition of a proton to the alkene to give a carbonium ion,³ while the abnormal addition of hydrogen bromide proceeds through a free-radical chain mechanism.⁴ The normal addition to isobutylene gives the *t*-butyl halide while the abnormal addition yields isobutyl bromide. While the carbonium ion mechanism is generally accepted in ionizing solvents, formation of free carbonium ions in non-ionizing solvents is doubtful. The addition of hydrogen chloride to isobutylene was therefore undertaken to throw some light on the mechanism of this reaction in particular, and of reactions of polar molecules in non-ionizing solvents in general. This work was interrupted by the War and there is little chance that it can be resumed in the near future. This paper

therefore does not represent a completed research.

Previous Work.—The failure to observe homogeneous vapor-phase additions of halogen acids to alkenes (which additions should be simple and non-ionic) has been accounted for by Kistiakowsky and Stauffer.⁵ They showed that the activation energies for the addition of hydrogen chloride and hydrogen bromide to isobutylene (29 and 23 kcal./mole, respectively) are high (resulting in very low rates at moderate temperatures), that the equilibria for the additions are unfavorable at high temperatures, but that the kinetics of the (presumably) bimolecular addition reaction are in no way abnormal. On the other hand, a dry, liquid mixture of isobutylene and hydrogen chloride reacts instantaneously^{6d} at 0°, within one minute at -78°. Propylene and the butenes react slower. As pointed out by Kistiakowsky and Stauffer, the rapid liquid phase reactions must proceed by a mechanism very different from that in the gas reactions.

Maass and his associates⁶ have been the principal contributors to our knowledge of these liquid-phase reactions. They studied the addition of hydrogen chloride to propylene in sealed glass bulbs, in the absence of water and solvents. Such

(1) This paper is based on the Ph. D. dissertation of J. J. Katz, June, 1942. A preliminary account of this work was presented to the Division of Organic Chemistry at the St. Louis Meeting of the American Chemical Society, April 9, 1941, a more detailed account at the Atlantic City Meeting, April 10, 1946.

(2) Present addresses: (a) General Laboratories, United States Rubber Company, Passaic, N. J.; (b) Argonne National Laboratory, Chicago, Illinois.

(3) Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931). Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," The Institute of Chemistry of Great Britain and Ireland, London, 1932. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 375.

(4) Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940); Vaughn, Rust and Evans, *J. Org. Chem.*, **7**, 477 (1942).

(5) Kistiakowsky and Stauffer, *J. Am. Chem. Soc.*, **59**, 165 (1937).

(6) (a) Maass and Wright, *ibid.*, **46**, 2604 (1924); (b) Maass and Sivertz, *ibid.*, **47**, 2883 (1925); (c) Coffin, Sutherland and Maass, *Can. J. Research*, **2**, 267 (1930); (d) Coffin and Maass, *ibid.*, **3**, 526 (1930); (e) Holder and Maass, *ibid.*, **16B**, 453 (1938); (f) A. G. Brown, Master's Thesis, McGill University (1938).

a 1:1 mixture reacts in a few days at 20°, half the propene being converted to isopropyl chloride, half to a hexyl chloride, and a quarter of the hydrogen chloride remaining unreacted. The side reaction discouraged kinetic studies. With twice as much hydrogen chloride, the reaction is ten to fifteen times as fast, and less hexyl chloride is formed.^{6b} Hydrogen bromide adds perhaps two hundred times as fast as hydrogen chloride, and the latter, without adding itself, accelerates the addition of hydrogen bromide.^{6a,b} Rates thus depend more on the concentration of halogen acid than of alkene.^{6d,e} The additions are strongly accelerated by small proportions of water but not much by glass surfaces.^{6b,6f,7} The rate of the hydrogen chloride-propylene reaction increases with temperature up to about 45°, but has a negative temperature coefficient between 45 and 70°, the critical temperature of the reaction mixture, where the addition becomes extremely slow and at least partly heterogeneous.^{6c} Melting points of halogen acid-alkene mixtures show that some pairs form 1:1 complexes (not the stable addition product). The alkenes which form these complexes most readily are the ones which add halogen acids most rapidly at ordinary temperatures.^{6a,d} Maass and co-workers are therefore of the opinion that the addition of a halogen acid proceeds through the unimolecular rearrangement of a 1:1 complex and through the interaction of two such complexes to give, respectively, isopropyl chloride and hexyl chloride.^{6c,f} Water is thought to accelerate the reaction because it also enters the complexes, making them more reactive.^{6f}

O'Connor, Baldinger, Vogt and Hennion studied the rate of addition of hydrogen chloride to cyclohexene and 3-hexene in solvents.⁸ Because of experimental difficulties, they concluded only that simple second order rate equations are not followed. High rates were obtained in hydrocarbon solvents such as heptane and xylene, very low rates in ether and dioxane, showing that the donor solvents form complexes with halogen acids and reduce their effective concentration. Similar results were obtained in addition of halogen acids to α -pinene.⁹

Experimental

Isobutylene and hydrogen chloride were chosen for the present study because the simpler alkenes do not react rapidly enough with hydrogen chloride and because the more reactive hydrogen bromide gives rise to an abnormal addition reaction.¹⁰ Heptane was chosen as solvent because of its availability, lack of polarity, and convenient boiling point. The reaction chosen had a convenient rate in heptane at 0° and proceeded cleanly without side reactions. Because of the difficulty in handling hydrogen chloride solutions without losses and the need for avoiding

as far as possible the use of stopcocks, lubricants and mercury, the reaction was followed in sealed glass dilatometers. Reaction mixtures were prepared on a vacuum line, distillations and condensations being carried out with solid carbon dioxide or liquid nitrogen.

Reagents.—Isobutylene was prepared by warming *t*-butyl alcohol with oxalic acid. Since repeated distillations in the line failed to remove all the water, the alkene was filtered through glass wool at -78°, using a system like that described by Roper.¹¹ The product thus obtained was free from opalescence at -78°. Hydrogen chloride was prepared from sodium chloride and sulfuric acid, scrubbed with concentrated sulfuric acid, and condensed in liquid nitrogen. It was then sublimed repeatedly in the line, discarding the first and last portions in each case. Heptane was obtained from the Eastman Kodak Co. and was fractionally distilled through a Podbielniak column; b. p. 98.3–98.5° (760 mm.), n_D^{20} 1.3880.

Vacuum Line.—The line shown in Fig. 1 was attached (through a liquid nitrogen trap) to a three-stage mercury vapor pump. A vacuum of 10^{-6} mm. was regularly obtained, as measured by a MacLeod gage between the trap and pump. The yoke shown in Fig. 2 was attached at ground joint A. Isobutylene and hydrogen chloride were stored in 5-liter bulbs which had been strongly heated under high vacuum. The manometer, the 1-liter bulb, B, and that portion of the line to the right of and below stopcocks C, D and E served to measure the reactants. This system was calibrated by evacuating it, filling it with hydrogen chloride at various pressures, condensing the gas in water, and titrating the solution. Allowances were made for variations in room temperature. In order to avoid distillation of mercury from the manometer into bulb B or the dilatometer when these were cold and at very low pressure, stopcock F was kept closed under these conditions except for brief intervals. For the same reason, when gas from the system to the right of stopcock C was condensed in the dilatometer, the pressure in the system was usually not allowed to drop below about 2 mm.; a correction was introduced for the remaining gas which was then rejected.

Dilatometers.—Figure 2 shows one of the dilatometers used. The volumes of the bulbs were about 25 ml. The diameters of the capillaries were about 2 mm., their volumes being 0.030 to 0.035 ml. per cm. of length. Liquid levels were read from a single brass scale, G, 17 cm. long, graduated in millimeters, and used on all the dilatometers. The glass saddle, H, fitted a notch in the bottom of the scale. A rubber band passing through notches in the scale and around hook, I, and another at the top, held the scale so that perfectly reproducible readings were obtained. The capillaries were tested for uniformity of bore and their diameters determined by calibration with mercury before they were attached to the bulbs. The use of safety bulbs (1–2 cc. capacity) at the tops of the capillaries was found to result in slow drainage of liquid and bubble formation in the capillaries.

Procedure.—Dilatometers were cleaned with warm acid chromate solution and rinsed thoroughly with water. Steam was then passed for several hours through a fine capillary extending into the bulbs of the inverted dilatometers. Dilatometers were then sealed at L onto the yoke shown in Fig. 2, and thus attached to the vacuum line at joint A, Fig. 1. Making allowances for the isobutylene and hydrogen chloride to be used, a quantity of heptane calculated to give a suitable scale reading at 0° on the dilatometer was pipetted into tube K and about a gram of phosphorus pentoxide was added to the liquid. Glass wool plugs and more drying agent were then inserted as shown (Fig. 2); the apparatus was evacuated, and the dilatometer was heated with a hand torch. The heptane was then distilled back and forth between tube K and the dilatometer until the solvent showed no opalescence (water) at -78°. Calcium sulfate, activated alumina, and magnesium perchlorate were also tried as drying agents but found less effective. With the heptane in tube K and

(7) Bruson and Riener, *J. Am. Chem. Soc.*, **67**, 1178 (1945), showed that water greatly accelerates the addition of hydrogen chloride to dicyclopentadiene.

(8) O'Connor, Baldinger, Vogt and Hennion, *J. Am. Chem. Soc.*, **61**, 1454 (1939).

(9) Hennion and Irwin, *ibid.*, **63**, 860 (1941).

(10) Mayo and Savoy, *ibid.*, **69**, 1348 (1947).

(11) Roper, *Ind. Eng. Chem., Anal. Ed.*, **9**, 414 (1937).

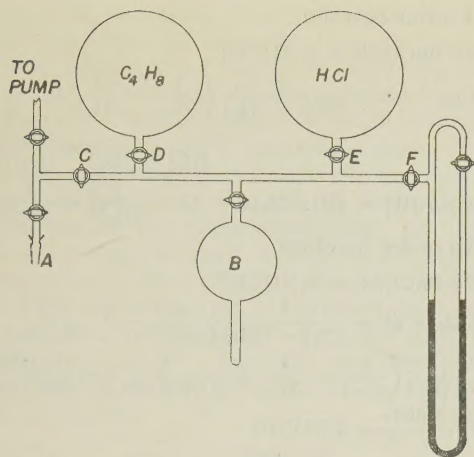


Fig. 1.—Apparatus for storing and measuring isobutylene and hydrogen chloride.

with stopcock M closed, isobutylene was condensed in the dilatometer. With the use of Dry Ice and then liquid nitrogen, heptane and finally hydrogen chloride, were condensed on top, this procedure helping to reduce premature reaction.* The dilatometer was then sealed off just above the capillary at L.

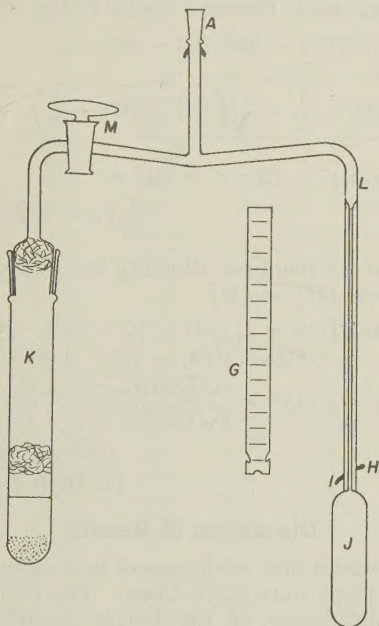


Fig. 2.—Dilatometer and yoke.

The dilatometer was removed from liquid nitrogen and warmed rapidly under running tap water to nearly 0° . When it was very cold, the dilatometer bulb contained about 2 cc. of free space, and during the warming period of about one minute, the dilatometer was shaken, inverted and spun repeatedly to mix the reactants and prevent later formation of bubbles in the capillary. The scale was then attached and the dilatometer was kept in a Dewar flask packed with crushed ice and water. The liquid level in the capillary would rise for a minute or two more, and after thermal equilibrium was reached in five to ten minutes the scale readings would decrease regularly, the total decrease for nearly complete reaction being around 8 cm.

The additions were usually about 90% complete in 3–5

weeks, and since it was impractical to let them proceed to completion, the final stage was determined by titration of the unreacted hydrogen chloride. Since it was desirable to preserve the dilatometers for future use, and since removal of the contents through the narrow stem without loss of hydrogen chloride was not simple, the apparatus shown in Fig. 3 was used. This device consisted of a glass tube (Q), fitted with a rubber stopper (N) and connections. The dilatometer capillary was notched with a file, inserted in rubber tubing (P), and broken at (O). By suitable manipulation of the screw clamps (S, T, U), the vessel (Q) was evacuated and the dilatometer was withdrawn from the tubing (P), so that the contents were discharged into ice water. When absorption of the hydrogen chloride was complete, the liquids were transferred to a separatory funnel and the aqueous layer was titrated with standard base. Blanks showed that the hydrolysis of tertiary butyl chloride under such conditions amounted to less than 0.5%.

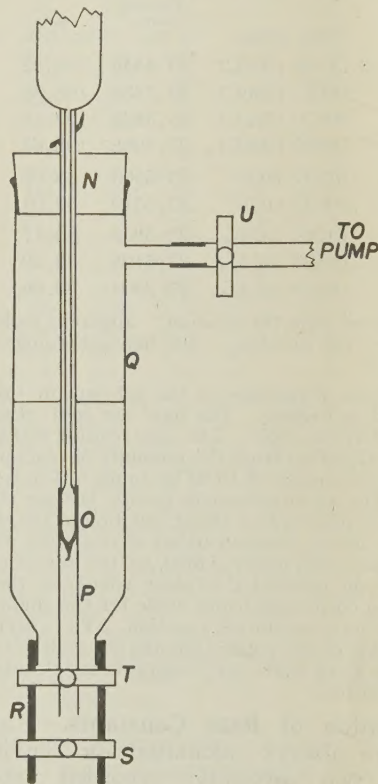


Fig. 3.—Apparatus for emptying dilatometers.

Absence of Side Reactions.—The reaction mixtures were reserved and combined for periodic recovery of the heptane. They were distilled through a Podbielniak column and found to contain *t*-butyl chloride (as expected), but there was no indication of the presence of other butyl chlorides nor of more than traces of material boiling above heptane.

Allowance for Premature Reaction.—In the preliminary experiments, it was assumed that the first dilatometer readings obtained after temperature equilibrium was reached represented closely the volume at 0% reaction. However, when the final extents of reaction were determined as described above and every experiment gave a different value for the volume decrease (7.7–15.1 cc.) per mole of *t*-butyl chloride formed, it became clear that considerable reaction occurred while the reaction mixture was warming from liquid nitrogen temperature to 0° . Three experiments were therefore terminated as soon as they reached thermal equilibrium at 0° , and were found to have

reacted to the extent of 35–55% during the warming period, the least reaction being associated with the shortest warming period. Three nearly identical experiments were then allowed to proceed nearly to completion. Comparisons of volumes of corresponding experiments gave volume decreases of 19.0, 19.0 and 20.7 cc./mole of *t*-butyl chloride formed, subject to some uncertainty from losses of hydrogen chloride before the apparatus in Fig. 3 was available. The most reliable values of the volume change per mole were obtained from the apparent molal volumes of the individual reactants and the product in heptane at 0°, as shown in Table I. The volume change was taken as 19.84 cc./mole.

TABLE I

APPARENT MOLAL VOLUMES (ϕ) OF *t*-BUTYL CHLORIDE, HYDROGEN CHLORIDE AND ISOBUTYLENE IN HEPTANE AT 0°

Vol. heptane, cc.	Moles solute	Volume soln., cc.	ϕ , ^a cc./mole	Average
21.8954	0.01426 <i>t</i> -BuCl	23.4446	108.62	
22.1754	.01073 <i>t</i> -BuCl	23.3438	108.86	
22.6514	.00670 <i>t</i> -BuCl	23.3833	109.19	
22.9912	.00382 <i>t</i> -BuCl	23.4068	108.83	108.88
23.0761	.01217 HCl	23.5503	38.95	
23.1991	.00912 HCl	23.5549	39.01	38.98
22.4791	.01242 <i>i</i> -C ₄ H ₈	23.5866	89.17	
22.8117	.00888 <i>i</i> -C ₄ H ₈	23.6108	89.99	
22.7329	.00619 <i>i</i> -C ₄ H ₈	23.2904	90.06	89.74

^a Calculated from the relation: apparent molal volume of solute = (vol. mixture – vol. heptane)/moles solute.

The extents of reaction in the subsequent tables were determined as follows. The final per cent. reaction was determined by titration. The scale reading at 0% reaction was then calculated from the amounts of reactants added and a volume change of 19.84 cc./mole of *t*-butyl chloride formed. For all intermediate points, the per cent. reaction was assumed to be a linear function of the scale readings. The initial concentrations of reactants were taken as the number of moles added to the reaction mixture divided by the calculated average volume of the reaction mixture, no correction being made for the slight contraction of the mixture during reaction. The effect of using a larger value of the volume change per mole is to increase slightly the third order rate constants for all intervals except the last one.

Calculation of Rate Constants.—Rate constants are always calculated for the intervals between two successive recorded extents of reaction. In the equations below, [H] and [U] will represent the concentrations of hydrogen chloride and unsaturated compound (isobutylene), *t* will indicate the time elapsed (in minutes) since the first scale reading was recorded, and the subscripts 1 and 2 refer to the beginning and end of an interval. The rate and equilibrium constants will be defined by the equations, the integrated forms being used for all calculations of rate constants.

Second order reaction

- (1) $d[t\text{-BuCl}]/dt = k_2[H][U]$
- (2) $k_2(t_2 - t_1) = \frac{1}{[H_1] - [U_1]} \ln \frac{[U_1][H_2]}{[H_1][U_2]}$
- (3) when $[H] = [U]$: $k_2(t_2 - t_1) = \frac{1}{[H_2]} - \frac{1}{[H_1]}$

Third order reaction

- (4) $d[t\text{-BuCl}]/dt = k_3[H]^2[U]$
- (5) $k_3(t_2 - t_1) = \frac{1}{[U_1] - [H_1]} \left(\frac{1}{[H_2]} - \frac{1}{[H_1]} + \frac{1}{[U_1] - [H_1]} \ln \frac{[U_1][H_2]}{[H_1][U_2]} \right)$
- (6) when $[H] = [U]$: $2k_3(t_2 - t_1) = \frac{1}{[H_2]^2} - \frac{1}{[H_1]^2}$

Fourth order reaction

- (7) $d[t\text{-BuCl}]/dt = k_4[H]^2[U]^2$
- (8) $k_4(t_2 - t_1) = \frac{1}{[U_1] - [H_1]} \left\{ \frac{-1}{[H_2][U_2]} + \frac{1}{[H_1][U_1]} + \frac{2}{[U_1] - [H_1]} \left(\frac{1}{[H_2]} - \frac{1}{[H_1]} + \frac{1}{[U_1] - [H_1]} \ln \frac{[U_1][H_2]}{[H_1][U_2]} \right) \right\}$
- (9) $\frac{d[t\text{-BuCl}]}{dt} = k_4[H]^2[U]$
- (10) $k_4(t_2 - t_1) = \frac{1}{2[H_1] - [U_1]} \left\{ -\frac{1}{[H_2]^2} + \frac{1}{[H_1]^2} + \frac{2}{[U_1] - [H_1]} \left(\frac{1}{[H_2]} - \frac{1}{[H_1]} + \frac{1}{[U_1] - [H_1]} \ln \frac{[U_1][H_2]}{[H_1][U_2]} \right) \right\}$
- (11) when $[H] = [U]$: $3k_4(t_2 - t_1) = \frac{1}{[H_2]^3} - \frac{1}{[H_1]^3}$

Complex formation, [C] being the concentration of 1:1 complex, [H] and [U] being the concentrations of reactants free and bound in the complex

$$(12) C = K([H] - [C])([U] - [C])$$

$$(13) C =$$

$$[H] + [U] + \frac{1}{K} - \sqrt{\left([H] + [U] + \frac{1}{K}\right)^2 - 4[H][U]}$$

$$(14) \text{ when } [H] = [U]: C = [H] + \frac{1}{2K} (1 - \sqrt{4K[H] + 1})$$

Fourth order reaction allowing for concentration of complex, $[H] = [U]$

$$(15) d[t\text{-BuCl}]/dt = k'_4([H] - [C])^3([U] - [C]) = k'_4/K[C]([H] - [C])^2 = k'_4([H] - [C])^4$$

$$(16) k'_4(t_2 - t_1)/4K^3 = \frac{\sqrt{4K[H_2] + 1} - 1/3}{(\sqrt{4K[H_2] + 1} - 1)^3} - \frac{\sqrt{4K[H_1] + 1} - 1/3}{(\sqrt{4K[H_1] + 1} - 1)^3}$$

Discussion of Results

In all, about fifty additions of hydrogen chloride to isobutylene were carried out. The first half did not employ some of the better techniques described in the Experimental Part, and although they are entirely consistent with those presented here, they will not be considered further. Of the other twenty-five experiments, seventeen contained no added catalyst and gave no indication of the presence of water, either at -78° (as cloudiness) or at 0° (as tiny areas of film on the dilatometer bulb). Six runs gave visible indication of moisture, in spite of precautions. The representatives of each kind of run were chosen almost at random for presentation here. The essential data and the calculated rate constants appear in Table II. To bring out the trends in the reactions, in-

stead of obscuring them, the rate constants are all calculated for the intervals between successive scale readings, *not* from the beginning of the reaction. The data are summarized in Figs. 4-7. There the rate constant for each interval (on a logarithmic scale) is plotted against the concentration of hydrogen chloride or isobutylene (which-ever is lower) at the end of that interval, and the points for each experiment are joined by lines. Thus, in Expt. 4, Fig. 5, the rate of reaction from a concentration of hydrogen chloride of 0.3266 mole/liter to a concentration of 0.2786 mole/liter corresponds to a second order rate constant of 0.00167. The rate from this point down to 0.2487 molar corresponds to a constant of 0.00122, etc.

TABLE II

APPARENT RATE CONSTANTS IN THE ADDITION OF HYDROGEN CHLORIDE [H] TO ISOBUTYLENE [U]^a

Expt.	<i>t</i> , min.	[HCl] or [C ₄ H ₉] ^a moles/l.	<i>k</i> ₂ × 10 ^{3b}	<i>k</i> ₃ × 10 ^{3c}	<i>k</i> ₄ × 10 ^{3d}	<i>k</i> ₅ × 10 ^{2e}	<i>k</i> ₆ × 10 ^{2f}
			[H] _i = [U] _i	[H] _i = [U] _i	[H] _i = [U] _i	[H] _i = [U] _i	[H] _i = [U] _i
1	0	0.3514*	[H] _i = 0.5111	[U] _i = 0.4710			
	94	.3160*	3.02	8.04	9.18	2.4	2.1
	248	.2756*	2.65	7.94	8.83	2.66	2.4
	1296	.1853*	1.43	5.44	6.47	2.50	2.09
	4396	.1158*	0.82	4.46	5.69	3.21	2.37
	11400	.0695*	.56	4.39	6.44	4.04	3.43
	33480	.0309*	.43	4.99	9.70	11.9	5.95
	0	.3042*	[H] _i = 0.4983	[U] _i = 0.4237			
	90	.2737*	3.24	8.89	11.2	2.96	2.47
	1069	.1584*	1.98	7.15	9.8	3.54	2.62
	2570	.1044*	1.37	6.81	10.8	5.41	3.39
	4272	.0783*	1.02	6.22	11.4	7.04	3.82
	7350	.0490*	1.11	8.18	18.3	19.6	6.04
	20400	.0108*	1.17	12.0	58.4	59.5	12.4
4	0	.3266	[H] _i = 0.3877	[U] _i = 0.6425			
	171	.2786	1.67	5.51	2.96	1.01	1.85
	350	.2487	1.22	4.65	2.37	0.899	1.75
	1025	.1876	0.89	4.13	1.88	.891	1.94
	2600	.1296	.57	3.70	1.39	.903	2.42
	9682	.0611	.31	3.59	0.89	1.056	4.43
	25900	.0174	.27	8.96	.93	3.17	33.2
5	0	.2224*	[H] _i = 0.6179	[U] _i = 0.4079			
	100	.1734*	6.12	15.1	31.4	7.73	3.76
	348	.1164*	4.56	13.8	32.5	9.43	3.70
	1099	.0514*	3.77	13.1	50.9	18.17	4.59
	2448	.0161*	3.56	14.9	13.3	57.45	6.24
6	0	.3913	[H] _i = 0.4596	[U] _i = 0.5160			
	93	.3237	4.95	13.7	12.2	3.4	3.9
	297	.2560	3.34	11.7	9.73	3.44	4.08
	1680	.1225	2.30	13.8	10.2	6.35	8.54
	3965	.0572	2.38	30.0	17.4	22.4	38.5
	15700	.0041	3.03	287	43.6	436.9	3960
^a [H] _i and [U] _i are the stoichiometric concentrations of hydrogen chloride and isobutylene before any reaction occurred. ^b Calculated from equation 3. ^c Calculated from equation 6. ^d Calculated from equation 11. ^e Calculated from Equation 2. ^f Calculated from equation 5. ^g Calculated from equation 5, interchanging [H] and [U] so that the rate depends on [C ₄ H ₉] ² [HCl]. ^h Calculated from equation 8. ⁱ Calculated from equation 10. ^j <i>t</i> -Butyl chloride to make 0.4418 mole/liter added initially. ^k Water present as evidenced by a distinct opalescence of the heptane at -78°. ^l A faint film of mercury was condensed in the dilatometer. Since the original black deposit soon became white, the metal reacted with hydrogen chloride. ^m About 3 mg. of phosphorus pentoxide added to dilatometer.							
7 ^j	0	.3189	[H] _i = [U] _i = 0.3189				
	280	.2601	2.53	8.84		3.09	
	980	.2020	1.58	6.94		3.07	
	2310	.1610	0.96	5.29		2.97	
	5260	.1138	.87	6.55		4.96	
	10713	.0836	.58	6.04		6.31	
	31300	.0457	.48	8.15		14.19	
8 ^k	0	.3565	[H] _i = [U] _i = 0.5011				
	25	.2915	25.04	78.0		24.43	
	172	.2536	3.48	12.9		4.74	
	346	.2258	2.79	11.7		4.90	
	726	.1813	2.86	14.2		7.10	
	1226	.1422	3.03	19.0		12.0	
	3208	.0759	3.10	31.4		32.6	
	12980	.0277	2.35	57.8		153	
9 ^l	0	.3936	[H] _i = [U] _i = 0.4977				
	59	.3440	6.20	16.9		4.61	
	206	.2967	3.15	10.0		3.11	
	1206	.1771	2.28	11.7		4.73	
	2742	.1065	2.44	18.3		14.05	
	7059	.0485	2.61	39.0		61.31	
	14200	.0257	2.56	76.2		234	
10 ^j	0	.4025	[H] _i = [U] _i = 0.5167				
	25	.3359	19.7	53.9		14.74	
	93	.2530	14.3	49.7		17.35	
	268	.1638	12.2	61.8		31.58	
	1375	.0521	11.8	150		206	
	3535	.0094	40.3	2530		18480	
11	0	.3900	[H] _i = [U] _i = 0.4954				
	110	.3246	4.70	13.3		3.75	
	397	.2477	3.33	11.9		4.24	
	1183	.1611	2.76	14.1		7.35	
	2582	.1005	2.68	21.6		17.77	
	10030	.0321	2.85	58.5		131	
	32130	.0109	2.74	168		1120	
12 ^m	0	.3466	[H] _i = [U] _i = 0.5000				
	43	.2881	13.6	43.3		13.80	
	116	.2271	12.8	50.3		19.9	
	252	.1667	11.7	61		32.0	
	1169	.0573	12.5	146		185	
	7068	.0057	26.8	2580		30480	

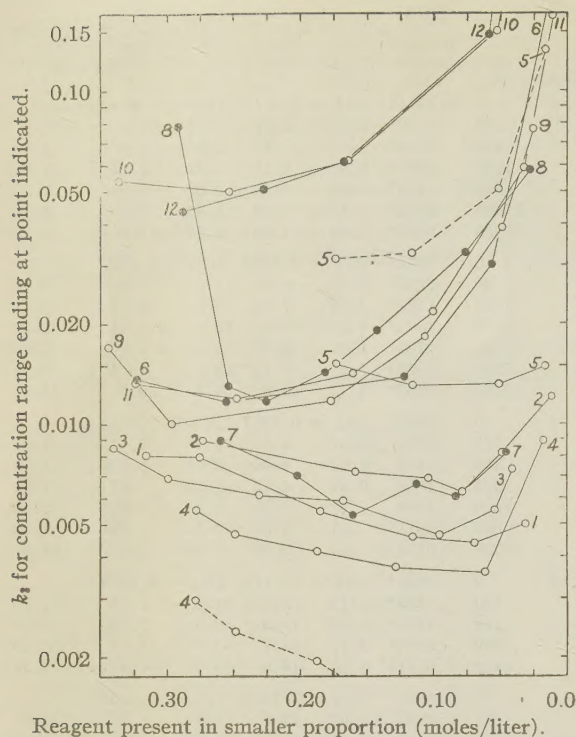


Fig. 4.—Third order rate constants for the addition of hydrogen chloride to isobutylene. Solid lines join points based on $[HCl]^2[C_4H_8]$; broken lines join points based on $[HCl][C_4H_8]^2$.

rapidly as the reaction progressed. The rate of decrease was probably very regular, the slight irregularities in the rate constant plots probably being due to the effect of very slight temperature changes on the dilatometer level. During the last interval, where the average concentration of reactants was 13% of that in the first interval, the rate of formation of *t*-butyl chloride was only 0.2% as great, the decrease corresponding closely to that expected for a third order reaction. However, k_3 tends to decrease slowly during the first 75% of the reaction (cf. Table II and Fig. 4), then to increase rather sharply to its initial value. The second order constant (Fig. 5) changes less in the last interval, while the fourth order constant (Fig. 6) changes less during the first 50% of the reaction. The apparent fourth order constant finally increases rapidly.

Figures 4–6 show that expts. 1, 2, 4, 5 and 7 behave much like expt. 3, but expts. 8–12 fall into another class. The latter group of runs was known to contain water or added traces of mercury or phosphoric acid (added as phosphorus pentoxide), all being possible trace impurities in any reaction mixture. These runs gave good second order rate constants over wide concentration ranges (Fig. 5) and sharply increasing constants of higher order (Figs. 4 and 6). The final rise in second order constants in expts. 10 and 12 may be due to the presence of a second phase or a surface re-

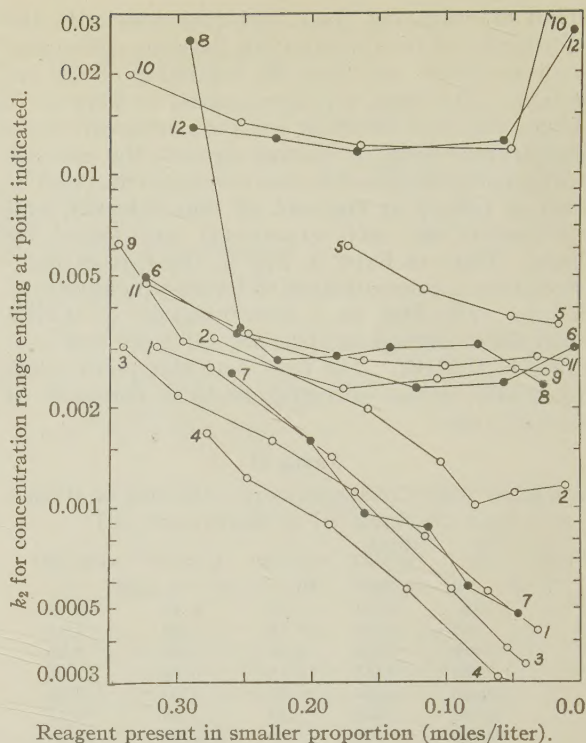


Fig. 5.—Second order rate constants for the addition of hydrogen chloride to isobutylene.

action. The apparent high rate constant for the first interval in expt. 8 is probably explained by a high initial dilatometer reading, due to rapid reaction and overheating. Suggestions of a similar effect appear in the first interval of a few other experiments, but the first stage of expt. 8 was by far the fastest reaction we have recorded. Experiment 6 is not known to have contained impurities, but its behavior (Figs. 4–6) definitely places it with 8–12. The accidental catalyst has obscured the usual lowering of second and third order rate constants by excess isobutylene.

The above results suggest that in every run there is competition between a catalyzed second order reaction and an uncatalyzed higher order reaction. The more catalyst that is present, the higher is the initial rate and the earlier the second order reaction predominates. Expts. 1–5 and 7 apparently have the least catalyst, and from Figs. 4 and 6 the catalyzed reaction seems to offer no important competition for the higher order reaction at reagent concentrations above 0.1 molar, while the continued downward drift in second order rate constants (Fig. 5) shows that even in this lower range the high order reaction is still important.

Let us therefore concentrate our attention on expts. 1–5 and 7 in the intervals where the concentrations of hydrogen chloride and isobutylene have not decreased below 0.1 molar. Table III lists the average rate constants for each run over these intervals and the average deviation of the

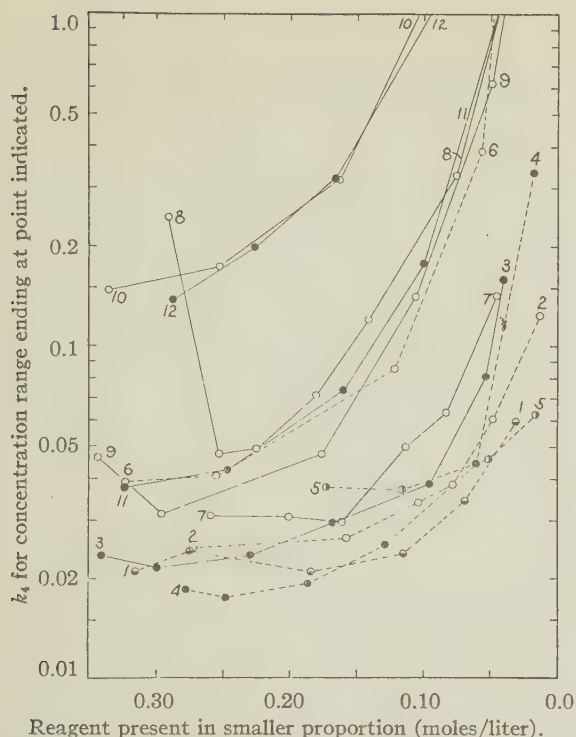


Fig. 6.—Fourth order rate constants for the addition of hydrogen chloride to isobutylene based on $[\text{HCl}]^3[\text{C}_4\text{H}_8]$. For comparison with Fig. 7, broken lines are used for experiments where concentrations of reagents were unequal.

constants for these intervals from the mean. Considering first the drift in constants in individual runs, we see that the largest drifts are in the second order rate constants, the smallest, in the fourth order rate constants calculated on $[\text{hydrogen chloride}]^3[\text{isobutylene}]$. Considering next the agreement between average constants for different runs, we see that for any order expt. 4 (with the largest excess of isobutylene) gives the smallest rate constants and that expt. 5 (with the largest excess of hydrogen chloride) gives the highest rate constants. Mean rate constants for the other four runs agree fairly well for any chosen order, the average deviation from the mean, about 15%, being largely a measure of the reproducibility of

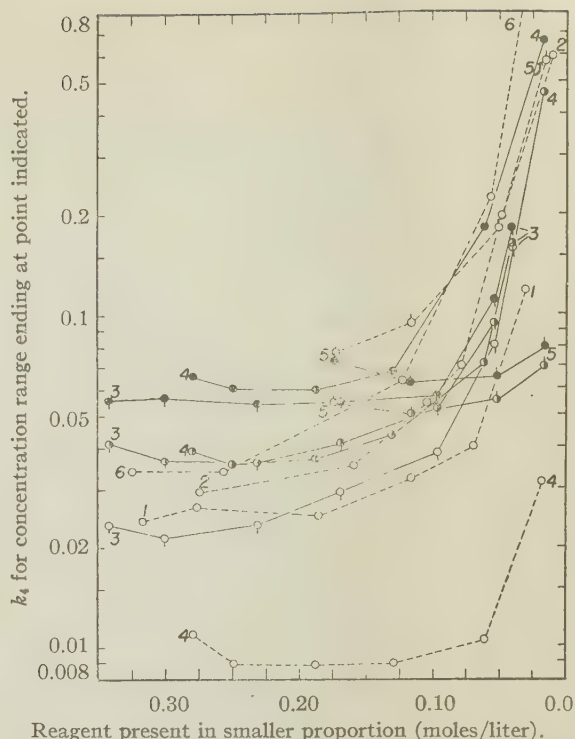


Fig. 7.—Fourth order rate constants for the addition of hydrogen chloride to isobutylene. For comparison with Fig. 6, the lowest line for expt. 3 duplicates the corresponding line in that figure and broken lines join points based on $[\text{HCl}]^2[\text{C}_4\text{H}_8]^2$ in experiments where concentrations of reagents were unequal. Solid lines join points for $[\text{HCl}]^3[\text{C}_4\text{H}_8]$ where the rate constants, but not the abscissae, are corrected for reagents bound in the hydrogen chloride-isobutylene complex, the equilibrium constant for its formation being taken either as 1/2 (half-shaded circles) or 1 (fully-shaded circles).

the experiments since all contained very similar initial concentrations of reactants. If we now compare the mean rate constants for expts. 4 and 5 with the averages from the other four experiments, we find that here also rate constants calculated on $[\text{hydrogen chloride}]^3[\text{isobutylene}]$ give the best fit, agreeing within about 30%, while any other basis in Table III shows differences by a factor of about 2 or more. The next best agreement is on constants based on $[\text{hydrogen chloride}]^2[\text{isobutylene}]$. Figures 4–6 point qualitatively to the same conclusions.

Complex Formation.—The most plausible interpretation of the observed high order of the additions (whether or not they are chain reactions) is that halogen acid-alkene complexes are involved, as proposed long ago by Maass and co-workers.⁶ The discussion thus far has been based on rate constants calculated according to equations 1–11, where the concentrations of reactants are the amounts initially put into the reaction mixtures less the amounts combined in *t*-butyl chloride. Equations 12–16 make allowance

TABLE III
MEAN RATE CONSTANTS FOR EXPTS. 1–5 AND 7 AT CONCENTRATIONS ABOVE 0.1 M

Expt.	$k_2 \times 10^3$ for $[\text{H}][\text{U}]$	$k_2 \times 10^3$ for $[\text{H}]^2[\text{U}]$	$k_2 \times 10^3$ for $[\text{H}][\text{U}]^2$	$k_4 \times 10^3$ for $[\text{H}]^2[\text{U}]^2$	$k_4 \times 10^3$ for $[\text{H}]^3[\text{U}]$
1	1.98(43) ^a	6.47(23) ^a	7.54(19) ^a	2.69(10) ^a	2.24(6.5) ^a
2	2.20(32)	7.62(11)	10.6(5.0)	3.97(24)	2.83(13)
3	1.98(32)	6.80(12)		2.44(10)	
4	1.09(33)	4.50(25)	2.15(24)	0.93(4.4)	1.99(11)
5	5.34(15)	14.45(4.5)	32.0(17)	8.58(10)	3.73(0.8)
7	1.48(38)	6.90(14)		3.52(20)	
Mean of 1, 2, 3, 7	1.91	6.95	7.96	3.15	2.76

^a Each figure in parentheses is mean deviation of rate constants, in per cent., from mean for that run.

for a reduction in the effective concentrations of reactants due to their partial combination in complexes.

No experimental values are available on the equilibrium constants but the following considerations will indicate their possible magnitude and the resulting corrections in the rate constants. In Fig. 6, expts. 3, 4 and 5 agree much better than on any other basis discussed previously. However, still better agreement can be obtained when the fourth order rate constants, k'_4 , are calculated from the concentrations of free reagents, using arbitrarily chosen values for the equilibrium constant, K , for complex formation. Results are summarized in Table IV and Fig. 7. Equation 16 was used to obtain k'_4 for expt. 3, but an integrated equation for expts. 4 and 5 was too difficult to develop. A differential equation might have been adequate for the present purpose, except at the final stages of the reaction, but instead the corrected rate constants, k'_4 , were calculated from the relation

$$(17) \quad k'_4 = k_4 \left(\frac{[\text{total HCl}]}{[\text{free HCl}]} \right)^3 \frac{[\text{total C}_4\text{H}_8]}{[\text{free C}_4\text{H}_8]}$$

Here, the k_4 values came from equation 10 and Table II; the total reagent concentrations were those at the ends of the corresponding intervals (as in Table II), and the concentrations of free reagents were calculated from equation 13, using

TABLE IV

FOURTH ORDER RATE CONSTANTS FOR THE ADDITION OF HYDROGEN CHLORIDE TO ISOBUTYLENE, CORRECTED FOR COMPLEX FORMATION

Expt.	[HCl] or [i-C ₄ H ₈]* ^a	C	$K = \frac{1}{2}$ $k'_4 \times 10^2$	C	$K = 1$ $k'_4 \times 10^2$
3	0.3409	0.0434	4.11	0.072	5.58
	.2998	.0348	3.64	.059	5.68
	.2304	.0214	3.62	.037	5.08
	.1685	.0120	4.13	.022	5.64
	.0966	.0044	5.23	.0076	5.75
	.0543	.0014	9.42	.0027	11.09
	.0404	.0008	16.21	.0015	18.35
	Mean ^b		3.87		5.49
	Deviation ^b		(6.3%)		(3.8%)
4	0.2786	0.054	3.92	0.086	6.56
	.2487	.0465	3.59	.075	6.04
	.1876	.0325	3.70	.053	5.97
	.1296	.0210	4.34	.0345	6.71
	.0611	.0085	7.12	.0150	10.82
	.0174	.0018	46.3	.0035	65.9
	Mean ^b		3.89		6.32
	Deviation ^b		(6.2%)		(5.0%)
5	.1734*	.026	5.46	.0442	6.27
	.1164*	.0165	5.03	.0272	6.26
	.0514*	.006	5.56	.0105	6.53
	.0161*	.0015	7.02	.0030	8.00
	Mean ^b		5.25		6.76
	Deviation ^b		(4.2%)		(7.4%)

* Concentration at end of interval, not corrected for complex formation. ^b For intervals where concentration of both reagents exceeds 0.1 *M*.

two values of K . This approximation corrects the rate constant over an interval by making a concentration correction which is exact only at the end of the interval. Both the apparent rate constants, k_4 and k'_4 , include K as a factor.

Several arbitrary values of K were tested but the best agreement between experiments was obtained with $K = 1/2$ and $K = 1$, a range which seems reasonable. Comparison of Tables II and IV and Figs. 6 and 7 shows that with these values of K , k'_4 is two to four times as large as k_4 at the beginning of expts. 3-5, but that k'_4 and k_4 approach the same value as the concentration of reagents, and the correction, approach zero. (The correction does not therefore improve the trend of second and third order rate constants.) The result is that the fourth order constants which tended to rise in Fig. 6 exhibit a smaller and delayed rise in Fig. 7. The mean deviations of the rate constants in Table IV do not show the full improvement since they are based only on the rate constants in the concentration range above 0.1 *M*. However, the most interesting result of the correction is the much better agreement brought about between expts. 4 and 5, with excesses of isobutylene or hydrogen chloride. Without the correction, the mean values of k_4 in expts. 4 and 5 differ from that in expt. 3 by an average of 31%, but with $K = 1/2$ and 1, the differences are only 18 and 12%, respectively. The largest effect of compound formation appears in expt. 4, where excess propylene reduces the effective concentration of hydrogen chloride which appears to the third power in the rate expression.

The Effect of Temperature.—One of the most striking features of the addition of hydrogen chloride to isobutylene is the higher rate observed after cooling a reaction mixture. Table V shows the effect of cooling and warming a reaction mixture after the rate had been established at 0°. During a fifteen-minute period consisting of a quick cooling to -78° and then a quick warming to 0°, the rate of reaction about doubled. Since a similar treatment with four and one-half hours of standing at -78° gave a reduced rate of reaction, the acceleration in the first experiment seemed to occur in the warming period. This conclusion was confirmed by cooling the reaction mixture quickly in liquid nitrogen, leaving it there for ten minutes and then allowing it to warm slowly (eighteen minutes) in air, with constant agitation. During this thirty-minute interval, the value of k_3 was about 600 times that in the preceding interval, 90 times that in the succeeding interval at 0°. The effect is even more surpris-

(12) As shown in Fig. 4, some increase in k_3 is common at the end of an addition. The rate constants cited in Table V suggest that the experiment is intermediate between the slow and fast groups of experiments in Fig. 4, but no cloudiness from water was observed. Several other experiments led to the same qualitative conclusions on the effects of cooling and warming. The largest effects appear when the concentrations of reactants are highest, at the beginning of an experiment.

ing when allowance is made for the facts that the reaction mixture was frozen solid for about half of the thirty-minute interval considered and that the second cooling period indicated a steady rate at -78° of about one-third the rate at 0° .

TABLE V

THE EFFECT OF TEMPERATURE ON THE ADDITION OF HYDROGEN CHLORIDE TO ISOBUTYLENE

$t_2 - t_1$ min.	[HCl] ^a	Reaction, %	$k_2 \times 10^3$ (Eq. 6)	Temperature
0	0.4126	22.13	$[H]_i = [U]_i = 0.5300$	
55	.3627	31.6	1.56	0°
90	.3160	40.4	1.34	0°
15	.3045	42.54	2.6	Quickly cooled to -78° , quickly warmed to 0°
105	.2742	48.26	1.20	0°
280	.2514	52.68	.45	Quickly cooled to -78° , left 4 hours, quickly warmed to 0°
305	.2107	60.27	.95	0°
725	.1639	69.08	1.01	0°
30	.0502	90.52	598	Quickly cooled to -195° , warmed slowly
9910	.0242	95.44	6.61	0°

^a At end of interval.

An attempt was made to account for this temporary acceleration of addition by a factor of 100–1000 during the warming period. Taking the third order rate constant for addition at -78° as one-third as large as at 0° , the equilibrium constant for complex formation at 0° as equal to or less than one, and the heat of complex formation as 5 kcal./mole or less, rates were calculated for an intermediate temperature. No calculation led to a significantly higher third order rate constant at -30° than at 0° , although a 15% rate increase could be anticipated for a fourth order reaction. Since there was no evidence of heterogeneity on cooling the reaction mixture, two alternatives seem to be left to account for the remarkable acceleration of the reaction on slow warming: (1) A cold reaction mixture presumably contains considerably more complex than a warm one, but the decomposition of the complex may be slow enough that when a mixture is warmed, an artificially high concentration of complex permits a temporarily higher rate of addition. (2) Somewhere in between -78 and 0° , conditions may be favorable for an exceptionally rapid addition by a chain mechanism, involving not free radicals but possibly carbonium ions. The polymerization of isobutylene by boron trifluoride proceeds at a high rate at very low temperatures¹³ but at a low rate above 0° . The polymerization of styrene by stannic chloride is of third to fourth order and has a very low activation energy¹⁴ but there are indications that these catalysts¹⁵ may

(13) Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.*, **62**, 276 (1940).

(14) Williams, *J. Chem. Soc.*, 1046 (1938); 775 (1940).

(15) Evans, Holden, Plesch, Polanyi, Skinner and Weinberger, *Nature*, **157**, 102 (1946); Evans, Meadows and Polanyi, *ibid.*, **158**, 94 (1946).

not be simple ones. Similar chain reactions may possibly occur in the addition of hydrogen chloride to isobutylene.

Conclusions.—This work has shown conclusively that the superficially simple addition of hydrogen chloride to isobutylene becomes very complex when it is investigated carefully in a non-ionizing solvent. Complexes and high order reactions of surprisingly low activation energy take the place of the relatively straight forward interactions which occur in hydroxylic solvents or in the vapor phase. Similar phenomena occur in the addition of hydrogen bromide to propylene.¹⁰ No evidence was found for a homogeneous, uncatalyzed bimolecular addition; this simplest reaction requires the most activation energy and occurs only at high temperatures.⁵

The tentative conclusion from the present work is that the uncatalyzed addition of hydrogen chloride to isobutylene in heptane solution is of third order with respect to hydrogen chloride and of first order with respect to isobutylene. However, since only integral orders have been tested, since the possibility of a chain reaction with complex kinetics has not been excluded, and since the reproducibility of the experiments leaves something to be desired, the results are not conclusive. Our conclusion is consistent with a reaction of a 1:1 complex of isobutylene and hydrogen chloride with a dimer of hydrogen chloride, or with the reaction of a 2:1 hydrogen chloride–alkene complex with hydrogen chloride. There is no direct evidence, however, for the existence of a 2:1 complex or a dimer of hydrogen chloride, although the latter should be a better proton donor than the monomer. Another possibility is that an indefinite number of hydrogen chloride molecules is associated with the reaction of a 1:1 hydrogen chloride–alkene complex, much as an indefinite number of water molecules is associated with the hydrolysis of *t*-butyl chloride.¹⁶ In such a case, the apparent activation energy of the reaction might well be expected to decrease as more hydrogen chloride becomes associated with the complex, accounting in part for the observed effects of temperature on the reaction rate.

In the presence of water, phosphoric acid or mercury chlorides, complexes apparently are formed with hydrogen chloride and the separation of charges in the addition of hydrogen chloride to isobutylene is easier; these catalysts take the place of excess hydrogen chloride in the high order reaction and the catalyzed reaction becomes of first order with respect to both hydrogen chloride and isobutylene. This type of addition is the one commonly observed in ionizing solvents.³

These results and conclusion parallel those obtained in this Laboratory on the cleavage of diethyl ether in ionizing and non-ionizing solvents.¹⁷ They serve to point out again our lack of informa-

(16) Hammett, "Physical Organic Chemistry," The McGraw-Hill Book Co., New York, N. Y., 1940, p. 169.

(17) Mayo, Hardy and Schultz, *J. Am. Chem. Soc.*, **63**, 426 (1941).

tion on the mechanism of presumably simple organic reactions under presumably simple conditions.

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Summary

The addition of hydrogen chloride to isobutylene in heptane solution at 0° was studied by a dilatometric method. *t*-Butyl chloride was the only product found. The addition was greatly accelerated by traces of water, mercury and phosphorus

pentoxide, all of which were difficult to exclude completely, and the experiments were therefore not entirely reproducible. The uncatalyzed reaction seems to be of third order with respect to hydrogen chloride and of first order with respect to isobutylene, while the catalyzed reaction approximates second order. An addition proceeding at 0° is greatly accelerated by cooling to -80° or below and then warming to 0° . The high order of the addition and the unusual effect of temperature can be accounted for if hydrogen chloride-isobutylene complexes are involved in the reaction, but the possibility that the addition is a chain mechanism of the ionic type has not been excluded.

